

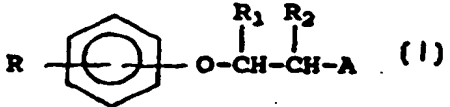
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(54) Title: POLYALKYLPHENOXYAMINOALKANES AND FUEL COMPOSITIONS CONTAINING THE SAME			
(57) Abstract			
<p>Polyalkylphenoxyaminoalkanes having formula (I), wherein R is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000; R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and A is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms. The compounds of formula (I) are useful as fuel additives for the prevention and control of engine deposits.</p>			
<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 10px;">R</div>  <div style="margin-left: 10px;">(1)</div> </div>			

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POLYALKYLPHENOXYAMINOALKANES  
AND FUEL COMPOSITIONS CONTAINING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to novel polyalkylphenoxyaminoalkanes. In a further aspect, this invention relates to the use of these compounds in fuel compositions to prevent and control engine deposits.

Description of the Related Art

It is well known that automobile engines tend to form deposits on the surface of engine components, such as carburetor ports, throttle bodies, fuel injectors, intake ports and intake valves, due to the oxidation and polymerization of hydrocarbon fuel. These deposits, even when present in relatively minor amounts, often cause noticeable driveability problems, such as stalling and poor acceleration. Moreover, engine deposits can significantly increase an automobile's fuel consumption and production of exhaust pollutants. Therefore, the development of effective fuel detergents or "deposit control" additives to prevent or control such deposits is of considerable importance and numerous such materials are known in the art.

For example, aliphatic hydrocarbon-substituted phenols are known to reduce engine deposits when used in fuel compositions. U.S. Patent No. 3,849,085, issued November 19, 1974 to Kreuz et al., discloses a motor fuel composition comprising a mixture of hydrocarbons in the gasoline boiling range containing about 0.01 to 0.25 volume

01 percent of a high molecular weight aliphatic  
02 hydrocarbon-substituted phenol in which the aliphatic  
03 hydrocarbon radical has an average molecular weight in the  
04 range of about 500 to 3,500. This patent teaches that  
05 gasoline compositions containing minor amounts of an  
06 aliphatic hydrocarbon-substituted phenol not only prevent or  
07 inhibit the formation of intake valve and port deposits in a  
08 gasoline engine, but also enhance the performance of the  
09 fuel composition in engines designed to operate at higher  
10 operating temperatures with a minimum of decomposition and  
11 deposit formation in the manifold of the engine.

12  
13 U.S. Patent No. 4,259,086, issued March 31, 1981 to  
14 Machleder et al., discloses a detergent additive for fuels  
15 and lubricating oils which comprises the reaction product of  
16 an aliphatic hydrocarbon-substituted phenol, epichlorohydrin  
17 and a primary or secondary monoamine or polyamine. In  
18 addition, U.S. Patent No. 4,048,081, issued September 13,  
19 1977 to Machleder et al., discloses a detergent additive for  
20 gasoline which is the reaction product of a polyisobutene  
21 phenol with epichlorohydrin, followed by amination with  
22 ethylene diamine or other polyamine.

23  
24 Similarly, U.S. Patent No. 4,134,846, issued January 16,  
25 1979 to Machleder et al., discloses a fuel additive  
26 composition comprising a mixture of (1) the reaction product  
27 of an aliphatic hydrocarbon-substituted phenol,  
28 epichlorohydrin and a primary or secondary mono- or  
29 polyamine, and (2) a polyalkylene phenol. This patent  
30 teaches that such compositions show excellent carburetor,  
31 induction system and combustion chamber detergency and, in  
32 addition, provide effective rust inhibition when used in  
33 hydrocarbon fuels at low concentrations.

34

01 Amino phenols are also known to function as  
02 detergents/dispersants, antioxidants and anti-corrosion  
03 agents when used in fuel compositions. U.S. Patent  
04 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for  
05 example, discloses amino phenols having at least one  
06 substantially saturated hydrocarbon-based substituent of at  
07 least 30 carbon atoms. The amino phenols of this patent are  
08 taught to impart useful and desirable properties to  
09 oil-based lubricants and normally liquid fuels.

10  
11 In addition, polybutylamines have been taught to be useful  
12 for preventing deposits in the intake system of internal  
13 combustion engines. For example, U.S. Patent No. 4,832,702,  
14 issued May 23, 1989 to Kummer et al., discloses fuel and  
15 lubricant compositions containing polybutyl or  
16 polyisobutylamine additives prepared by hydroformulating a  
17 polybutene or polyisobutene and then subjecting the  
18 resulting oxo product to a Mannich reaction or amination  
19 under hydrogenating conditions.

20  
21 Polyether amine fuel additives are also well known in the  
22 art for the prevention and control of engine deposits.  
23 These polyether additives have a polyoxyalkylene "backbone",  
24 i.e., the polyether portion of the molecule consists of  
25 repeating oxyalkylene units. U.S. Patent No. 4,191,537,  
26 issued March 4, 1980 to Lewis et al., for example, discloses  
27 a fuel composition comprising a major portion of  
28 hydrocarbons boiling in the gasoline range and from 30 to  
29 2,000 ppm of a hydrocarbyl polyoxyalkylene aminocarbamate  
30 having a molecular weight from about 600 to 10,000, and at  
31 least one basic nitrogen atom. The hydrocarbyl  
32 polyoxyalkylene moiety is composed of oxyalkylene units  
33 having from 2 to 5 carbon atoms in each oxyalkylene unit.  
34 These fuel compositions are taught to maintain the

01 cleanliness of intake systems without contributing to  
02 combustion chamber deposits.  
03  
04 Aromatic compounds containing a poly(oxyalkylene) moiety are  
05 also known in the art. For example, the above-mentioned U.S.  
06 Patent No. 4,191,537, discloses alkylphenyl  
07 poly(oxyalkylene) polymers which are useful as intermediates  
08 in the preparation of alkylphenyl poly(oxyalkylene)  
09 aminocarbamates.  
10  
11 Similarly, U.S. Patent No. 4,881,945, issued November 21,  
12 1989 to Buckley, discloses a fuel composition comprising a  
13 hydrocarbon boiling in the gasoline or diesel range and from  
14 about 30 to about 5,000 parts per million of a fuel soluble  
15 alkylphenyl polyoxyalkylene aminocarbamate having at least  
16 one basic nitrogen and an average molecular weight of about  
17 800 to 6,000 and wherein the alkyl group contains at least  
18 40 carbon atoms.  
19  
20 U.S. Patent No. 5,112,364, issued May 12, 1992 to Rath et  
21 al., discloses gasoline-engine fuels which contain small  
22 amounts of a polyetheramine and/or a polyetheramine  
23 derivative, wherein the polyetheramine is prepared by  
24 reductive amination of a phenol-initiated or alkylphenol-  
25 initiated polyether alcohol with ammonia or a primary amine.  
26  
27 European Patent Application Publication No. 310,875,  
28 published April 12, 1989 discloses fuels for spark ignition  
29 engines containing a polyetheramine additive prepared by  
30 first propoxylating and/or butoxylating an alkanol or  
31 primary or secondary alkylmonoamine and then aminating the  
32 resulting polyether with ammonia or a primary aliphatic  
33 amine.  
34

01 French Patent No. 2,105,539, published April 28, 1972,  
02 discloses carburetor detergent additives which are  
03 phenoxypropylamines which may be substituted with up to five  
04 hydrocarbon radicals of 1 to 30 carbon atoms on the aromatic  
05 ring. This patent also discloses additives obtained by  
06 reacting such phenoxypropylamines with alkylphosphoric  
07 acids.

08

09

SUMMARY OF THE INVENTION

10

11 I have now discovered certain polyalkylphenoxyaminoalkanes  
12 which provide excellent control of engine deposits,  
13 especially intake valve deposits, when employed as fuel  
14 additives in fuel compositions.

15

16 The compounds of the present invention include those having  
17 the following formula and fuel soluble salts thereof:

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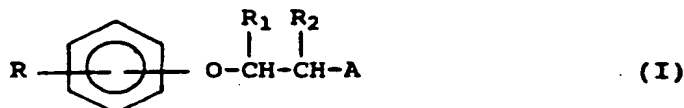
24 wherein R is a polyalkyl group having an average molecular  
25 weight in the range of about 600 to 5,000;

26

27 R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or lower alkyl having 1  
28 to 6 carbon atoms; and

29

30 A is amino, N-alkyl amino having about 1 to about 20 carbon  
31 atoms in the alkyl group, N,N-dialkyl amino having about 1  
32 to about 20 carbon atoms in each alkyl group, or a polyamine  
33 moiety having about 2 to about 12 amine nitrogen atoms and  
34 about 2 to about 40 carbon atoms.



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01 The present invention further provides a fuel composition  
02 comprising a major amount of hydrocarbons boiling in the  
03 gasoline or diesel range and a deposit-controlling effective  
04 amount of a compound of the present invention.

05

06 The present invention additionally provides a fuel  
07 concentrate comprising an inert stable oleophilic organic  
08 solvent boiling in the range of from about 150°F. to 400°F.  
09 and from about 10 to 70 weight percent of a compound of the  
10 present invention.

11

12 Among other factors, the present invention is  
13 based on the surprising discovery that certain  
14 polyalkylphenoxyaminoalkanes provide excellent  
15 control of engine deposits, especially on intake valves,  
16 when employed as additives in fuel compositions.

17

18 DETAILED DESCRIPTION OF THE INVENTION

19

20 The polyalkylphenoxyaminoalkanes of the present invention  
21 have the general formula:

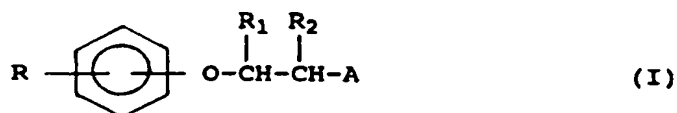
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wherein R, R<sub>1</sub>, R<sub>2</sub> and A are as defined above.

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Preferably, R is a polyalkyl group having an average  
molecular weight in the range of about 600 to 3,000, more  
preferably about 700 to 3,000, and most preferably about 900  
to 2,500.



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01 Preferably, one of R<sub>1</sub> and R<sub>2</sub> is hydrogen or lower alkyl of 1  
02 to 4 carbon atoms, and the other is hydrogen. More  
03 preferably, one of R<sub>1</sub> and R<sub>2</sub> is hydrogen, methyl or ethyl,  
04 and the other is hydrogen. Most preferably, R<sub>2</sub> is hydrogen,  
05 methyl or ethyl, and R<sub>1</sub> is hydrogen.

06  
07 In general, A is amino, N-alkyl amino having from about 1 to  
08 about 20 carbon atoms in the alkyl group, preferably about 1  
09 to about 6 carbon atoms, more preferably about 1 to about 4  
10 carbon atoms; N,N-dialkyl amino having from about 1 to about  
11 20 carbon atoms in each alkyl group, preferably about 1 to  
12 about 6 carbon atoms, more preferably about 1 to about 4  
13 carbon atoms; or a polyamine moiety having from about 2 to  
14 about 12 amine nitrogen atoms and from about 2 to about 40  
15 carbon atoms, preferably about 2 to 12 amine nitrogen atoms  
16 and about 2 to 24 carbon atoms. More preferably, A is amino  
17 or a polyamine moiety derived from a polyalkylene polyamine,  
18 including alkylene diamine. Most preferably, A is amino or  
19 a polyamine moiety derived from ethylene diamine or  
20 diethylene triamine.

21  
22 It is preferred that the R substituent is located at the  
23 meta or, more preferably, the para position on the aromatic  
24 ring, i.e., para or meta relative to the ether group.

25  
26 The compounds of the present invention will generally have a  
27 sufficient molecular weight so as to be non-volatile at  
28 normal engine intake valve operating temperatures (about  
29 200°-250°C.). Typically, the molecular weight of the  
30 compounds of this invention will range from about 700 to  
31 about 3,500, preferably from about 700 to about 2,500.

32  
33  
34

01 Fuel-soluble salts of the compounds of formula I can be  
02 readily prepared for those compounds containing an amino or  
03 substituted amino group and such salts are contemplated to  
04 be useful for preventing or controlling engine deposits.  
05 Suitable salts include, for example, those obtained by  
06 protonating the amino moiety with a strong organic acid,  
07 such as an alkyl- or arylsulfonic acid. Preferred salts are  
08 derived from toluenesulfonic acid and methanesulfonic acid.

09

10 Definitions

11

12 As used herein, the following terms have the following  
13 meanings unless expressly stated to the contrary.

14

15 The term "amino" refers to the group:  $-NH_2$ .

16

17 The term "N-alkylamino" refers to the group:  $-NHR_a$  wherein  
18  $R_a$  is an alkyl group. The term "N,N-dialkylamino" refers to  
19 the group:  $-NR_bR_c$ , wherein  $R_b$  and  $R_c$  are alkyl groups.

20

21 The term "hydrocarbyl" refers to an organic radical  
22 primarily composed of carbon and hydrogen which may be  
23 aliphatic, alicyclic, aromatic or combinations thereof,  
24 e.g., aralkyl or alkaryl. Such hydrocarbyl groups are  
25 generally free of aliphatic unsaturation, i.e., olefinic or  
26 acetylenic unsaturation, but may contain minor amounts of  
27 heteroatoms, such as oxygen or nitrogen, or halogens, such  
28 as chlorine.

29

30 The term "alkyl" refers to both straight- and branched-chain  
31 alkyl groups.

32

33

34

01 The term "lower alkyl" refers to alkyl groups having 1 to  
02 about 6 carbon atoms and includes primary, secondary and  
03 tertiary alkyl groups. Typical lower alkyl groups include,  
04 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,  
05 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

06  
07 The term "polyalkyl" refers to an alkyl group which is  
08 generally derived from polyolefins which are polymers or  
09 copolymers of mono-olefins, particularly 1-mono-olefins,  
10 such as ethylene, propylene, butylene, and the like.  
11 Preferably, the mono-olefin employed will have 2 to about  
12 24 carbon atoms, and more preferably, about 3 to 12 carbon  
13 atoms. More preferred mono-olefins include propylene,  
14 butylene, particularly isobutylene, 1-octene and 1-decene.  
15 Polyolefins prepared from such mono-olefins include  
16 polypropylene, polybutene, especially polyisobutene, and the  
17 polyalphaolefins produced from 1-octene and 1-decene.

18  
19 The term "fuel" or "hydrocarbon fuel" refers to normally  
20 liquid hydrocarbons having boiling points in the range of  
21 gasoline and diesel fuels.

## 22 23 General Synthetic Procedures

24  
25 The polyalkylphenoxyaminoalkanes of this invention may be  
26 prepared by the following general methods and procedures.  
27 It should be appreciated that where typical or preferred  
28 process conditions (e.g., reaction temperatures, times, mole  
29 ratios of reactants, solvents, pressures, etc.) are given,  
30 other process conditions may also be used unless otherwise  
31 stated. Optimum reaction conditions may vary with the  
32 particular reactants or solvents used, but such conditions  
33 can be determined by one skilled in the art by routine  
34 optimization procedures.

01 Those skilled in the art will also recognize that it may be  
02 necessary to block or protect certain functional groups  
03 while conducting the following synthetic procedures. In  
04 such cases, the protecting group will serve to protect the  
05 functional group from undesired reactions or to block its  
06 undesired reaction with other functional groups or with the  
07 reagents used to carry out the desired chemical  
08 transformations. The proper choice of a protecting group  
09 for a particular functional group will be readily apparent  
10 to one skilled in the art. Various protecting groups and  
11 their introduction and removal are described, for example,  
12 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*  
13 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,  
14 and references cited therein.

15

16 Synthesis

17

18 The polyalkylphenoxyminoalkanes of the present invention  
19 may be prepared by a process which initially involves  
20 hydroxyalkylation of a polyalkylphenol of the formula:

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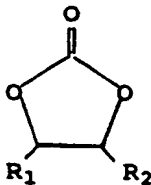
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(II)

wherein R is as defined herein, with an alkylene carbonate  
of the formula:



(III)

01 wherein  $R_1$  and  $R_2$  are as defined herein, in the presence of  
02 a catalytic amount of an alkali metal hydride or hydroxide,  
03 or alkali metal salt, to provide a polyalkylphenoxyalkanol  
04 of the formula:

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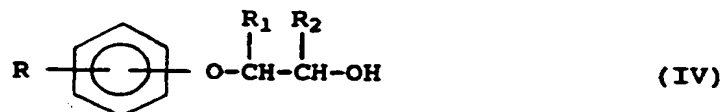
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34



wherein  $R$ ,  $R_1$  and  $R_2$  are as defined herein.

The polyalkylphenols of formula II are well known materials and are typically prepared by the alkylation of phenol with the desired polyolefin or chlorinated polyolefin. A further discussion of polyalkylphenols can be found, for example, in U.S. Patent No. 4,744,921 and U.S. Patent No. 5,300,701.

Accordingly, the polyalkylphenols of formula II may be prepared from the corresponding olefins by conventional procedures. For example, the polyalkylphenols of formula II above may be prepared by reacting the appropriate olefin or olefin mixture with phenol in the presence of an alkylating catalyst at a temperature of from about 25°C. to 150°C., and preferably 30°C. to 100°C. either neat or in an essentially inert solvent at atmospheric pressure. A preferred alkylating catalyst is boron trifluoride. Molar ratios of reactants may be used. Alternatively, molar excesses of phenol can be employed, i.e., 2 to 3 equivalents of phenol for each equivalent of olefin with unreacted phenol recycled. The latter process maximizes monoalkylphenol. Examples of inert solvents include heptane, benzene, toluene, chlorobenzene and 250 thinner which is a mixture of aromatics, paraffins and naphthenes.

01 The polyalkyl substituent on the polyalkylphenols employed  
02 in the invention is generally derived from polyolefins which  
03 are polymers or copolymers of mono-olefins, particularly  
04 1-mono-olefins, such as ethylene, propylene, butylene, and  
05 the like. Preferably, the mono-olefin employed will have 2  
06 to about 24 carbon atoms, and more preferably, about 3 to 12  
07 carbon atoms. More preferred mono-olefins include  
08 propylene, butylene, particularly isobutylene, 1-octene and  
09 1-decene. Polyolefins prepared from such mono-olefins  
10 include polypropylene, polybutene, especially polyisobutene,  
11 and the polyalphaolefins produced from 1-octene and  
12 1-decene.

13  
14 The preferred polyisobutenes used to prepare the presently  
15 employed polyalkylphenols are polyisobutenes which comprise  
16 at least about 20% of the more reactive methylvinylidene  
17 isomer, preferably at least 50% and more preferably at least  
18 70%. Suitable polyisobutenes include those prepared using  
19  $\text{BF}_3$  catalysts. The preparation of such polyisobutenes in  
20 which the methylvinylidene isomer comprises a high  
21 percentage of the total composition is described in U.S.  
22 Patent Nos. 4,152,499 and 4,605,808. Such polyisobutenes,  
23 known as "reactive" polyisobutenes, yield high molecular  
24 weight alcohols in which the hydroxyl group is at or near  
25 the end of the hydrocarbon chain. Examples of suitable  
26 polyisobutenes having a high alkylvinylidene content include  
27 Ultravis 30, a polyisobutene having a number average  
28 molecular weight of about 1300 and a methylvinylidene  
29 content of about 74%, and Ultravis 10, a polyisobutene  
30 having a number average molecular weight of about 950 and a  
31 methylvinylidene content of about 76%, both available from  
32 British Petroleum.

33  
34

01 The alkylene carbonates of formula III are known compounds  
02 which are available commercially or can be readily prepared  
03 using conventional procedures. Suitable alkylene carbonates  
04 include ethylene carbonate, propylene carbonate, 1,2-  
05 butylene carbonate, 2,3-butylene carbonate, and the like. A  
06 preferred alkylene carbonate is ethylene carbonate.

07  
08 The catalyst employed in the reaction of the polyalkylphenol  
09 and alkylene carbonate may be any of the well known  
10 hydroxyalkylation catalysts. Typical hydroxyalkylation  
11 catalysts include alkali metal hydrides, such as lithium  
12 hydride, sodium hydride and potassium hydride, alkali metal  
13 hydroxides, such as sodium hydroxide and potassium  
14 hydroxide, and alkali metal salts, for example, alkali metal  
15 halides, such as sodium chloride and potassium chloride, and  
16 alkali metal carbonates, such as sodium carbonate and  
17 potassium carbonate. The amount of catalyst employed will  
18 generally range from about 0.01 to 1.0 equivalent,  
19 preferably from about 0.05 to 0.3 equivalent.

20  
21 The polyalkylphenol and alkylene carbonate are generally  
22 reacted in essentially equivalent amounts in the presence of  
23 the hydroxyalkylation catalyst at a temperature in the range  
24 of about 100°C. to 210°C., and preferably from about 150°C.  
25 to about 170°C. The reaction may take place in the presence  
26 or absence of an inert solvent.

27  
28 The time of reaction will vary depending on the particular  
29 alkylphenol and alkylene carbonate reactants, the catalyst  
30 used and the reaction temperature. Generally, the reaction  
31 time will range from about two hours to about five hours.  
32 The progress of the reaction is typically monitored by the  
33 evolution of carbon dioxide. At the completion of the  
34

01 reaction, the polyalkylphenoxyalkanol product is isolated  
02 using conventional techniques.

03

04 The hydroxyalkylation reaction of phenols with alkylene  
05 carbonates is well known in the art and is described, for  
06 example, in U.S. Patent Nos. 2,987,555; 2,967,892; 3,283,030  
07 and 4,341,905.

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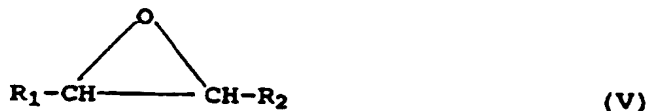
09 Alternatively, the polyalkylphenoxyalkanol product of  
10 formula IV may be prepared by reacting the polyalkylphenol  
11 of formula II with an alkylene oxide of the formula:

12

13

14

15



16

17 wherein R<sub>1</sub> and R<sub>2</sub> are as defined herein, in the presence of  
18 a hydroxyalkylation catalyst as described above.

19

20 Suitable alkylene oxides of formula V include ethylene  
21 oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene  
22 oxide, and the like. A preferred alkylene oxide is ethylene  
23 oxide.

24

25 In a manner similar to the reaction with alkylene carbonate,  
26 the polyalkylphenol and alkylene oxide are reacted in  
27 essentially equivalent or equimolar amounts in the presence  
28 of 0.01 to 1.0 equivalent of a hydroxyalkylation catalyst,  
29 such as sodium or potassium hydride, at a temperature in the  
30 range of about 30°C. to about 150°C., for about 2 to about  
31 24 hours. The reaction may be conducted in the presence or  
32 absence of a substantially anhydrous inert solvent.

33 Suitable solvents include toluene, xylene, and the like.

34 Generally, the reaction is conducted at a pressure



01 sufficient to contain the reactants and any solvent present,  
02 typically at atmospheric or higher pressure. Upon  
03 completion of the reaction, the polyalkylphenoxyalkanol is  
04 isolated by conventional procedures.

05

06 The polyalkylphenoxyalkanol of formula IV is subsequently  
07 reacted, either directly or through an intermediate, with an  
08 appropriate amine to provide the desired  
09 polyalkylphenoxyaminoalkanes of formula I. Suitable amine  
10 reactants which may be employed to form the amine component,  
11 i.e., substituent A, of the polyalkylphenoxyaminoalkanes of  
12 the present invention are discussed more fully below.

13

#### 14 The Amine Component

15

16 In general, the amine component of the present  
17 polyalkylphenoxyaminoalkanes will contain an average of at  
18 least about one basic nitrogen atom per molecule. A "basic  
19 nitrogen atom" is one that is titratable by a strong acid,  
20 for example, a primary, secondary, or tertiary amine  
21 nitrogen; as distinguished from, for example, an carbamyl  
22 nitrogen, e.g., -OC(O)NH-, which is not titratable with a  
23 strong acid. Preferably, at least one of the basic nitrogen  
24 atoms of the amine component will be primary or secondary  
25 amine nitrogen, more preferably, at least one will be a  
26 primary amine nitrogen.

27

28 The amine component of the polyalkylphenoxyaminoalkanes of  
29 this invention is preferably derived from ammonia, a primary  
30 alkyl or secondary dialkyl monoamine, or a polyamine having  
31 a terminal amino nitrogen atom.

32

33 Primary alkyl monoamines useful in preparing compounds of  
34 the present invention contain 1 nitrogen atom and from about

01 1 to about 20 carbon atoms, more preferably about 1 to 6  
02 carbon atoms, most preferably 1 to 4 carbon atoms. Examples  
03 of suitable monoamines include *N*-methylamine, *N*-ethylamine,  
04 *N*-*n*-propylamine, *N*-isopropylamine, *N*-*n*-butylamine, *N*-  
05 isobutylamine, *N*-sec-butylamine, *N*-tert-butylamine, *N*-*n*-  
06 pentylamine, *N*-cyclopentylamine, *N*-*n*-hexylamine, *N*-  
07 cyclohexylamine, *N*-octylamine, *N*-decylamine, *N*-dodecylamine,  
08 *N*-octadecylamine, *N*-benzylamine, *N*-(2-phenylethyl)amine, 2-  
09 aminoethanol, 3-amino-1-propanol, 2-(2-aminoethoxy)ethanol,  
10 *N*-(2-methoxyethyl)amine, *N*-(2-ethoxyethyl)amine and the  
11 like. Preferred primary amines are *N*-methylamine,  
12 *N*-ethylamine and *N*-*n*-propylamine.

13  
14 The amine component of the present  
15 polyalkylphenoxyaminoalkanes may also be derived from a  
16 secondary dialkyl monoamine. The alkyl groups of the  
17 secondary amine may be the same or different and will  
18 generally each contain about 1 to about 20 carbon atoms,  
19 more preferably about 1 to about 6 carbon atoms, most  
20 preferably about 1 to about 4 carbon atoms. One or both of  
21 the alkyl groups may also contain one or more oxygen atoms.

22  
23 Preferably, the alkyl groups of the secondary amine are  
24 independently selected from the group consisting of methyl,  
25 ethyl, propyl, butyl, pentyl, hexyl, 2-hydroxyethyl and 2-  
26 methoxyethyl. More preferably, the alkyl groups are methyl,  
27 ethyl or propyl.

28  
29 Typical secondary amines which may be used in this invention  
30 include *N,N*-dimethylamine, *N,N*-diethylamine, *N,N*-di-*n*-  
31 propylamine, *N,N*-diisopropylamine, *N,N*-di-*n*-butylamine,  
32 *N,N*-di-sec-butylamine, *N,N*-di-*n*-pentylamine, *N,N*-di-*n*-  
33 hexylamine, *N,N*-dicyclohexylamine, *N,N*-dioctylamine,  
34 *N*-ethyl-*N*-methylamine, *N*-methyl-*N*-*n*-propylamine, *N*-*n*-butyl-

01 N-methylamine, N-methyl-N-octylamine, N-ethyl-N-  
02 isopropylamine, N-ethyl-N-octylamine, N,N-di(2-  
03 hydroxyethyl)amine, N,N-di(3-hydroxypropyl)amine,  
04 N,N-di(ethoxyethyl)amine, N,N-di(propoxyethyl)amine and the  
05 like. Preferred secondary amines are N,N-dimethylamine,  
06 N,N-diethylamine and N,N-di-n-propylamine.

07  
08 Cyclic secondary amines may also be employed to form the  
09 additives of this invention. In such cyclic compounds, the  
10 alkyl groups, when taken together, form one or more 5- or  
11 6-membered rings containing up to about 20 carbon atoms.  
12 The ring containing the amine nitrogen atom is generally  
13 saturated, but may be fused to one or more saturated or  
14 unsaturated rings. The rings may be substituted with  
15 hydrocarbyl groups of from 1 to about 10 carbon atoms and  
16 may contain one or more oxygen atoms.

17  
18 Suitable cyclic secondary amines include piperidine,  
19 4-methylpiperidine, pyrrolidine, morpholine,  
20 2,6-dimethylmorpholine and the like.

21  
22 Suitable polyamines can have a straight- or branched-chain  
23 structure and may be cyclic or acyclic or combinations  
24 thereof. Generally, the amine nitrogen atoms of such  
25 polyamines will be separated from one another by at least  
26 two carbon atoms, i.e., polyamines having an amina  
27 structure are not suitable. The polyamine may also contain  
28 one or more oxygen atoms, typically present as an ether or a  
29 hydroxyl group. Polyamines having a carbon-to-nitrogen ratio  
30 of from about 1:1 to about 10:1 are particularly preferred.

31  
32 In preparing the compounds of this invention using a  
33 polyamine where the various nitrogen atoms of the polyamine  
34 are not geometrically equivalent, several substitutional

01 isomers are possible and each of these possible isomers is  
02 encompassed within this invention.

03

04 A particularly preferred group of polyamines for use in the  
05 present invention are polyalkylene polyamines, including  
06 alkylene diamines. Such polyalkylene polyamines will  
07 typically contain from about 2 to about 12 nitrogen atoms  
08 and from about 2 to about 40 carbon atoms, preferably about  
09 2 to 24 carbon atoms. Preferably, the alkylene groups of  
10 such polyalkylene polyamines will contain from about 2 to  
11 about 6 carbon atoms, more preferably from about 2 to about  
12 4 carbon atoms.

13

14 Examples of suitable polyalkylene polyamines include  
15 ethylenediamine, propylenediamine, isopropylenediamine,  
16 butylenediamine, pentylenediamine, hexylenediamine,  
17 diethylenetriamine, dipropylenetriamine,  
18 dimethylaminopropylamine, diisopropylenetriamine,  
19 dibutylenetriamine, di-sec-butylenetriamine,  
20 triethylenetetraamine, tripropylenetetraamine,  
21 triisobutylenetetraamine, tetraethylenepentamine,  
22 pentaethylenhexamine, dimethylaminopropylamine, and  
23 mixtures thereof.

24

25 Particularly suitable polyalkylene polyamines are those  
26 having the formula:

27



29

30 wherein  $\text{R}_3$  is a straight- or branched-chain alkylene group  
31 having from about 2 to about 6 carbon atoms, preferably from  
32 about 2 to about 4 carbon atoms, most preferably about 2  
33 carbon atoms, i.e., ethylene ( $-\text{CH}_2\text{CH}_2-$ ); and  $z$  is an integer  
34 from about 1 to about 4, preferably about 1 or about 2.

01 Particularly preferred polyalkylene polyamines are  
02 ethylenediamine, diethylenetriamine, triethylenetetraamine,  
03 and tetraethylenepentamine. Most preferred are  
04 ethylenediamine and diethylenetriamine, especially  
05 ethylenediamine.

06  
07 Also contemplated for use in the present invention are  
08 cyclic polyamines having one or more 5- to 6-membered rings.  
09 Such cyclic polyamines compounds include piperazine,  
10 2-methylpiperazine, N-(2-aminoethyl)piperazine,  
11 N-(2-hydroxyethyl)piperazine, 1,2-bis-(N-piperaziny)ethane,  
12 3-aminopyrrolidine, N-(2-aminoethyl)pyrrolidine, and the  
13 like. Among the cyclic polyamines, the piperazines are  
14 preferred.

15  
16 Many of the polyamines suitable for use in the present  
17 invention are commercially available and others may be  
18 prepared by methods which are well known in the art. For  
19 example, methods for preparing amines and their reactions  
20 are detailed in Sidgewick's "The Organic Chemistry of  
21 Nitrogen", Clarendon Press, Oxford, 1966; Noller's  
22 "Chemistry of Organic Compounds", Saunders, Philadelphia,  
23 2nd Ed., 1957; and Kirk-Othmer's "Encyclopedia of Chemical  
24 Technology", 2nd Ed., especially Volume 2, pp. 99-116.

25  
26 Preparation of the Polyalkylphenoxyaminoalkane

27  
28 As noted above, the polyalkylphenoxyaminoalkanes of the  
29 present invention may be conveniently prepared by reacting  
30 the polyalkylphenoxyalkanol of formula IV, either directly  
31 or through an intermediate, with a nitrogen-containing  
32 compound, such as ammonia, a primary or secondary alkyl  
33 monoamine, or a polyamine, as described herein.

34

01 Accordingly, the polyalkylphenoxyalkanol of formula IV may  
02 be converted to the desired polyalkylphenoxyaminoalkane by a  
03 variety of procedures known in the art.

04

05 For example, the terminal hydroxy group on the  
06 polyalkylphenoxyalkanol may first be converted to a suitable  
07 leaving group, such as a mesylate, chloride or bromide, and  
08 the like, by reaction with a suitable reagent, such as  
09 methanesulfonyl chloride. The resulting  
10 polyalkylphenoxyalkyl mesylate or equivalent intermediate  
11 may then be converted to a phthalimide derivative by  
12 reaction with potassium phthalimide in the presence of a  
13 suitable solvent, such as *N,N*-dimethylformamide. The  
14 polyalkylphenoxyalkyl phthalimide derivative is subsequently  
15 converted to the desired polyalkylphenoxyaminoalkane by  
16 reaction with a suitable amine, such as hydrazine.  
17 Alternatively, the leaving group can be converted to an  
18 azide, as described, for example, in Turnbull Scriven,  
19 Chemical Reviews, Volume 88, pages 297-368, 1988. The azide  
20 is subsequently converted to the desired  
21 polyalkylphenoxyaminoalkane by reduction with hydrogen and a  
22 catalyst, such as palladium on carbon or a Lindlar catalyst.

23

24 The polyalkylphenoxyalkanol of formula IV may also be  
25 converted to the corresponding polyalkylphenoxyalkyl  
26 chloride by reaction with a suitable halogenating agent,  
27 such as HCl, thionyl chloride, or epichlorohydrin, followed  
28 by displacement of the chloride with a suitable amine, such  
29 as ammonia, a primary or secondary alkyl monoamine, or a  
30 polyamine, as described, for example, in U.S. Patent No.  
31 4,247,301 to Honnen, the disclosure of which is incorporated  
32 herein by reference.

33

34

01 Alternatively, the polyalkylphenoxyaminoalkanes of the  
02 present invention may be prepared from the corresponding  
03 polyalkylphenoxyalkanol by a process commonly referred to as  
04 reductive amination, such as described in U.S. Patent No.  
05 5,112,364 to Rath et al. and U.S. Patent No. 4,332,595 to  
06 Herbstman et al., the disclosures of which are incorporated  
07 herein by reference.

08

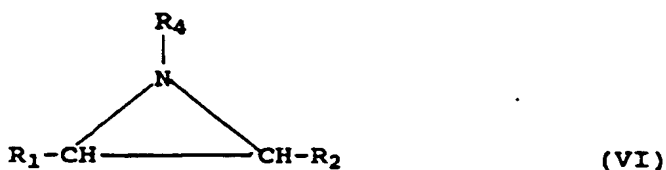
09 In the reductive amination procedure, the  
10 polyalkylphenoxyalkanol is aminated with an appropriate  
11 amine, such as ammonia or a primary alkyl monoamine, in the  
12 presence of hydrogen and a hydrogenation-dehydrogenation  
13 catalyst. The amination reaction is typically carried out  
14 at temperatures in the range of about 160°C to about 250°C  
15 and pressures of about 1,000 to about 5,000 psig, preferably  
16 about 1,500 to about 3,000 psig. Suitable hydrogenation-  
17 dehydrogenation catalysts include those containing platinum,  
18 palladium, cobalt, nickel, copper, or chromium, or mixtures  
19 thereof. Generally, an excess of the ammonia or amine  
20 reactant is used, such as about a 5-fold to about 60-fold  
21 molar excess, and preferably about a 10-fold to about 40-  
22 fold molar excess, of ammonia or amine.

23

24 When the reductive amination is carried out with a polyamine  
25 reactant, the amination is preferably conducted using a two-  
26 step procedure as described in commonly-assigned copending  
27 U.S. Patent application Serial No. 08/574,485, filed  
28 December 19, 1995, and titled, "Reductive Amination Process  
29 for Manufacturing a Fuel Additive From Polyoxybutylene  
30 Alcohol with Ethylene Diamine", the disclosure of which is  
31 incorporated herein by reference in its entirety. According  
32 to this procedure, an appropriate alcohol is first contacted  
33 with a hydrogenation-dehydrogenation catalyst at a  
34 temperature of at least 230°C to provide a carbonyl-

01 containing intermediate, which is subsequently reacted with  
02 a polyamine at a temperature below about 190°C in the  
03 presence of hydrogen and a hydrogenation catalyst to produce  
04 the desired polyamine adduct.

05  
06 In an alternative procedure for preparing the  
07 polyalkylphenoxyaminoalkanes of the present invention, the  
08 polyalkylphenol of formula II may be reacted with an  
09 aziridine of the formula:



16 wherein R<sub>1</sub> and R<sub>2</sub> are as defined herein, and R<sub>4</sub> is hydrogen  
17 or alkyl of 1 to 20 carbon atoms. A preferred aziridine is  
18 one wherein R<sub>1</sub> is hydrogen, R<sub>2</sub> is hydrogen, methyl or ethyl,  
19 and R<sub>4</sub> is hydrogen.

20  
21 The reaction of aziridines with alcohols to produce beta-  
22 amino ethers is well known in the art and is discussed, for  
23 example, in Ham and Dermer, "Ethyleneimine and Other  
24 Aziridines", Academic Press, New York, 1969, pages 224-227  
25 and 256-257.

26

27

#### Fuel Compositions

28

29 The compounds of the present invention are useful as  
30 additives in hydrocarbon fuels to prevent and control engine  
31 deposits, particularly intake valve deposits. The proper  
32 concentration of additive necessary to achieve the desired  
33 deposit control varies depending upon the type of fuel

34



01 employed, the type of engine, and the presence of other fuel  
02 additives.

03

04 In general, the concentration of the compounds of this  
05 invention in hydrocarbon fuel will range from about 50 to  
06 about 2500 parts per million (ppm) by weight, preferably  
07 from 75 to 1,000 ppm. When other deposit control additives  
08 are present, a lesser amount of the present additive may be  
09 used.

10

11 The compounds of the present invention may be formulated as  
12 a concentrate using an inert stable oleophilic (i.e.,  
13 dissolves in gasoline) organic solvent boiling in the range  
14 of about 150°F. to 400°F. (about 65°C. to 205°C.).

15 Preferably, an aliphatic or an aromatic hydrocarbon solvent  
16 is used, such as benzene, toluene, xylene or higher-boiling  
17 aromatics or aromatic thinners. Aliphatic alcohols  
18 containing about 3 to 8 carbon atoms, such as isopropanol,  
19 isobutylcarbinol, n-butanol and the like, in combination  
20 with hydrocarbon solvents are also suitable for use with the  
21 present additives. In the concentrate, the amount of the  
22 additive will generally range from about 10 to about  
23 70 weight percent, preferably 10 to 50 weight percent, more  
24 preferably from 20 to 40 weight percent.

25 In gasoline fuels, other fuel additives may be employed with  
26 the additives of the present invention, including, for  
27 example, oxygenates, such as t-butyl methyl ether, antiknock  
28 agents, such as methylcyclopentadienyl manganese  
29 tricarbonyl, and other dispersants/detergents, such as  
30 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines,  
31 hydrocarbyl poly(oxyalkylene) aminocarbamates, or  
32 succinimides. Additionally, antioxidants, metal  
33 deactivators and demulsifiers may be present.

34

01 In diesel fuels, other well-known additives can be employed,  
02 such as pour point depressants, flow improvers, cetane  
03 improvers, and the like.

04

05 A fuel-soluble, nonvolatile carrier fluid or oil may also be  
06 used with the compounds of this invention. The carrier  
07 fluid is a chemically inert hydrocarbon-soluble liquid  
08 vehicle which substantially increases the nonvolatile  
09 residue (NVR), or solvent-free liquid fraction of the fuel  
10 additive composition while not overwhelmingly contributing  
11 to octane requirement increase. The carrier fluid may be a  
12 natural or synthetic oil, such as mineral oil, refined  
13 petroleum oils, synthetic polyalkanes and alkenes, including  
14 hydrogenated and unhydrogenated polyalphaolefins, and  
15 synthetic polyoxyalkylene-derived oils, such as those  
16 described, for example, in U.S. Patent No. 4,191,537 to  
17 Lewis, and polyesters, such as those described, for example,  
18 in U.S. Patent Nos. 3,756,793 to Robinson and 5,004,478 to  
19 Vogel et al., and in European Patent Application  
20 Nos. 356,726, published March 7, 1990, and 382,159,  
21 published August 16, 1990.

22

23 These carrier fluids are believed to act as a carrier for  
24 the fuel additives of the present invention and to assist in  
25 removing and retarding deposits. The carrier fluid may also  
26 exhibit synergistic deposit control properties when used in  
27 combination with a compound of this invention.

28

29 The carrier fluids are typically employed in amounts ranging  
30 from about 100 to about 5000 ppm by weight of the  
31 hydrocarbon fuel, preferably from 400 to 3000 ppm of the  
32 fuel. Preferably, the ratio of carrier fluid to deposit  
33 control additive will range from about 0.5:1 to about 10:1,  
34 more preferably from 1:1 to 4:1, most preferably about 2:1.

01 When employed in a fuel concentrate, carrier fluids will  
02 generally be present in amounts ranging from about 20 to  
03 about 60 weight percent, preferably from 30 to 50 weight  
04 percent.

05

06

#### PREPARATIONS AND EXAMPLES

07

08 A further understanding of the invention can be had in the  
09 following nonlimiting Examples. Wherein unless expressly  
10 stated to the contrary, all temperatures and temperature  
11 ranges refer to the Centigrade system and the term "ambient"  
12 or "room temperature" refers to about 20°C.-25°C. The term  
13 "percent" or "%" refers to weight percent and the term  
14 "mole" or "moles" refers to gram moles. The term  
15 "equivalent" refers to a quantity of reagent equal in moles,  
16 to the moles of the preceding or succeeding reactant recited  
17 in that example in terms of finite moles or finite weight or  
18 volume. Where given, proton-magnetic resonance spectrum  
19 (p.m.r. or n.m.r.) were determined at 300 MHz, signals are  
20 assigned as singlets (s), broad singlets (bs), doublets (d),  
21 double doublets (dd), triplets (t), double triplets (dt),  
22 quartets (q), and multiplets (m), and cps refers to cycles  
23 per second.

24

25

#### Example 1

26

27

#### Preparation of Polyisobutyl Phenol

28

29 To a flask equipped with a magnetic stirrer, reflux  
30 condenser, thermometer, addition funnel and nitrogen inlet  
31 was added 203.2 grams of phenol. The phenol was warmed to  
32 40°C. and the heat source was removed. Then, 73.5

33

34

-26-

01 milliliters of boron trifluoride etherate was added  
02 dropwise. 1040 grams of Ultravis 10 Polyisobutene  
03 (molecular weight 950, 76% methylvinylidene, available from  
04 British Petroleum) was dissolved in 1,863 milliliters of  
05 hexane. The polyisobutene was added to the reaction at a  
06 rate to maintain the temperature between 22°C-27°C. The  
07 reaction mixture was stirred for 16 hours at room  
08 temperature. Then, 400 milliliters of concentrated ammonium  
09 hydroxide was added, followed by 2,000 milliliters of  
10 hexane. The reaction mixture was washed with water (3 X  
11 2,000 milliliters), dried over magnesium sulfate, filtered  
12 and the solvents removed under vacuum to yield 1,056.5 grams  
13 of a crude reaction product. The crude reaction product was  
14 determined to contain 80% of the desired product by proton  
15 NMR and chromatography on silica gel eluting with hexane,  
16 followed by hexane: ethylacetate: ethanol (93:5:2).

17

18

Example 2

19

20

Preparation of

21

22

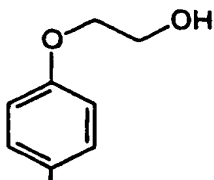
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27



28

PIB (molecular weight ~ 950)

29

30

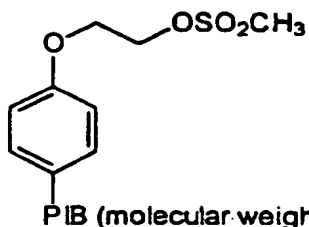
31 Potassium hydride (1.1 grams of a 35 weight percent  
32 dispersion of in mineral oil) and 4- polyisobutyl phenol  
33 (99.7 grams, prepared as in Example 1) were added to a  
34 flask equipped with a magnetic stirrer, reflux condensor,  
nitrogen inlet and thermometer. The reaction was heated at

-27-

01 130°C for one hour and then cooled to 100°C. Ethylene  
02 carbonate (8.6 grams) was added and the mixture was heated  
03 at 160°C for 16 hours. The reaction was cooled to room  
04 temperature and one milliliter of isopropanol was added.  
05 The reaction was diluted with one liter of hexane, washed  
06 three times with water and once with brine. The organic  
07 layer was dried over anhydrous magnesium sulfate, filtered  
08 and the solvents removed in vacuo to yield 98.0 grams of the  
09 desired product as a yellow oil.

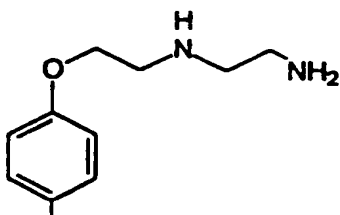
10  
11 Example 3

12  
13 Preparation of



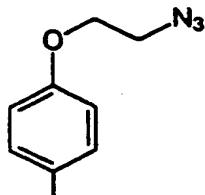
22 The alcohol from Example 2 (20.0 grams), triethylamine (2.9  
23 mL), and anhydrous dichloromethane (200 mL) were combined.  
24 The solution was cooled to 0°C and methanesulfonyl chloride  
25 (1.5 mL) was added dropwise. The reaction was stirred at  
26 room temperature under nitrogen for 16 hours. The solution  
27 was diluted with dichloromethane (600 mL) and was washed  
28 twice with saturated aqueous sodium bicarbonate solution and  
29 once with brine. The organic layer was dried over anhydrous  
30 sodium sulfate, filtered and the solvents removed in vacuo  
31 to yield 20.4 grams as a yellow oil.  
32  
33  
34

-28-

Example 4Preparation of

PB (molecular weight ~ 950)

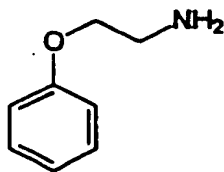
Ethylenediamine (12.3 mL) and anhydrous toluene (100 mL) were combined under nitrogen. The product from Example 3 (20.4 grams, dissolved in 100 mL of anhydrous toluene) was added dropwise. The resulting solution was refluxed for 16 hours. The solution was diluted with hexane (600 mL) and was washed once with saturated aqueous sodium bicarbonate solution, three times with water and once with brine. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvents removed in vacuo to yield 15.1 grams as a yellow oil. The oil was chromatographed on silica gel, eluting with hexane / diethyl ether (50:50) then hexane / diethyl ether / methanol / isopropylamine (40:40:15:5) to yield 10.3 grams of the desired product as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.25 (d, 2H), 6.8 (d, 2H), 4.1 (t, 2H), 3.0 (t, 2H), 2.85 (t, 2H), 2.75 (t, 2H), 1.95 (bs, 3H), 1.5-0.7 (m, 137H).

Example 5Preparation of

PIB (molecular weight ~ 950)

A mesylate prepared as described in Example 3 (406.5 grams), sodium azide (198.2 grams), Adogen 464, a methyltrialkyl (C<sub>8</sub>-C<sub>10</sub>) ammonium chloride available from Ashland Chemical (8.0 mL), N,N - dimethylformamide (800 mL) and toluene (1.2 L) were combined. The reaction was refluxed for sixteen hours and cooled to room temperature. The mixture was filtered and the solvent was removed in vacuo. The residue was diluted with hexane (3.0 L) and washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 334.3 grams of the desired azide as a yellow oil.

-30-

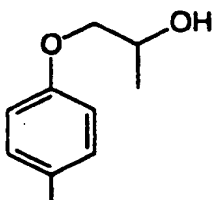
Example 6Preparation of

PIB (molecular weight ~ 950)

A solution of the product from Example 5 ( 334.3 grams ) in ethyl acetate (750 mL ) and toluene (750 mL ), containing 10% palladium on charcoal ( 7.0 grams ) was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low pressure hydrogenator. Catalyst filtration and removal of the solvent *in vacuo* yielded 322.3 grams of the desired product as a yellow oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.25 (d, 2H), 6.8 (d, 2H ), 4.0 (t, 1H), 3.1 (t, 2H), 2.35 (bs, 2H), 0.7-1.6 (m, 137H).

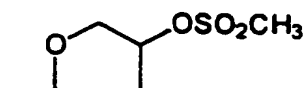


-31-

Example 7Preparation of

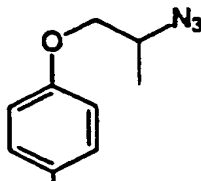
PIB (molecular weight ~ 950)

Potassium hydride (15.1 grams of a 35 weight percent dispersion of in mineral oil) and 4- polyisobutyl phenol (1378.5 grams, prepared as in Example 1) were added to a flask equipped with a mechanical stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Propylene carbonate (115.7 milliliters) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and ten milliliters of isopropanol were added. The reaction was diluted with ten liters of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 1301.7 grams of the desired product as a yellow oil.

Example 8Preparation of

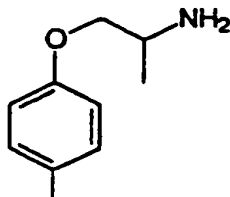
PB (molecular weight ~ 950)

The alcohol from Example 7 (50.0 grams), triethylamine (7.0 mL), and anhydrous dichloromethane (500 mL) were combined. The solution was cooled to 0°C and methanesulfonyl chloride (3.7 mL) was added dropwise. The reaction was stirred at room temperature under nitrogen for 16 hours. The solution was diluted with dichloromethane (1.5L) and was washed three times with saturated aqueous sodium bicarbonate solution and once with brine. The organic layer was dried over anhydrous sodium sulfate, filtered and the solvents removed in vacuo to yield 57.7 grams as a yellow oil.

Example 9Preparation of

PIB (molecular weight ~ 950)

The mesylate from Example 8 (57.7 grams ), sodium azide (27.1 grams ), Adogen 464 (1.0 mL ), N,N - dimethylformamide (400 mL ) and toluene (600 mL ) were combined. The reaction was refluxed for sixteen hours and cooled to room temperature. The mixture was filtered and the solvent was removed in vacuo . The residue was diluted with hexane (1.5 L ) and washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 43.1 grams of the desired azide as a yellow oil.

Example 10Preparation of

PB (molecular weight ~ 950)

A solution of the product from Example 9 ( 43.1 grams ) in ethyl acetate (100 mL ) and toluene (100 mL ), containing 10% palladium on charcoal ( 2.0 grams ) was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low pressure hydrogenator. Catalyst filtration and removal of the solvent *in vacuo* yielded 41.5 grams of the desired product as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.25 (d, 2H), 6.85 (d, 2H), 3.9 (abq, 1H), 3.65 (abq, 1H), 3.35 (m, 1H), 1.9 (bs, 2H), 0.7-1.6 (m, 140H).

Example 11Single-Cylinder Engine Test

The test compounds were blended in gasoline and their deposit reducing capacity determined in an ASTM/CFR single-cylinder engine test.

A Waukesha CFR single-cylinder engine was used. Each run was carried out for 15 hours, at the end of which time the intake valve was removed, washed with hexane and weighed.

01 The previously determined weight of the clean valve was  
02 subtracted from the weight of the valve at the end of the  
03 run. The differences between the two weights is the weight  
04 of the deposit. A lesser amount of deposit indicates a  
05 superior additive. The operating conditions of the test  
06 were as follows: water jacket temperature 200°F; vacuum of  
07 12 in Hg, air-fuel ratio of 12, ignition spark timing of  
08 400 BTC; engine speed is 1800 rpm; the crankcase oil is a  
09 commercial 30W oil.

10  
11 The amount of carbonaceous deposit in milligrams on the  
12 intake valves is reported for each of the test compounds in  
13 Table I and Table II.

14 TABLE I

15

16 Intake Valve Deposit Weight

17 (in milligrams)

18 Sample <sup>1</sup>	19 Run 1	20 Run 2	21 Average
22 Base Fuel	23 333.5	24 354.9	25 344.2
26 Example 4	27 22.5	28 22.7	29 22.6

30 <sup>1</sup>At 150 parts per million actives (ppma).

31 TABLE II

32

33 Intake Valve Deposit Weight

34 (in milligrams)

35 Sample <sup>1</sup>	36 Run 1	37 Run 2	38 Average
39 Base Fuel	40 323.8	41 312.1	42 318.0
43 Example 6	44 12.1	45 21.0	46 16.6

47 <sup>1</sup>At 125 parts per million actives (ppma).

01 The base fuel employed in the above single-cylinder engine  
02 tests was a regular octane unleaded gasoline containing no  
03 fuel detergent. The test compounds were admixed with the  
04 base fuel to give the concentrations indicated in the  
05 tables.

06  
07 The data in Table I and Table II illustrates the significant  
08 reduction in intake valve deposits provided by the  
09 polyalkylphenoxyaminoalkanes of the present invention  
10 (Examples 4 and 6) compared to the base fuel.  
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01 WHAT IS CLAIMED IS:

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03 1. A compound of the formula:

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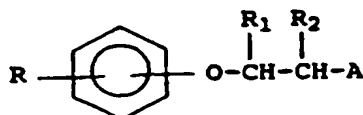
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or a fuel-soluble salt thereof, wherein R is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000;

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16

$R_1$  and  $R_2$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

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23

A is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms.

24

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2. The compound according to Claim 1, wherein one of  $R_1$  and  $R_2$  is hydrogen or lower alkyl of 1 to 4 carbon atoms, and the other is hydrogen.

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3. The compound according to Claim 2, wherein one of  $R_1$  and  $R_2$  is hydrogen, methyl or ethyl, and the other is hydrogen.

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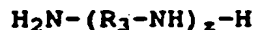
4. The compound according to Claim 3, wherein  $R_2$  is hydrogen, methyl or ethyl, and  $R_1$  is hydrogen.

- 01 5. The compound according to Claim 1, wherein R is a  
02 polyalkyl group having an average molecular weight in  
03 the range of about 600 to 3,000.
- 04 6. The compound according to Claim 5, wherein R is a  
05 polyalkyl group having an average molecular weight in  
06 the range of about 700 to 3,000.
- 07
- 08 7. The compound according to Claim 6, wherein R is a  
09 polyalkyl group having an average molecular weight in  
10 the range of about 900 to 2,500.
- 11
- 12 8. The compound according to Claim 1, wherein R is a  
13 polyalkyl group derived from polypropylene, polybutene,  
14 or a polyalphaolefin oligomer of 1-octene or 1-decene.
- 15
- 16 9. The compound according to Claim 8, wherein R is a  
17 polyalkyl group derived from polyisobutene.
- 18
- 19 10. The compound according to Claim 9, wherein the  
20 polyisobutene contains at least about 20% of a  
21 methylvinylidene isomer.
- 22
- 23 11. The compound according to Claim 1, wherein A is amino,  
24 N-alkyl amino or a polyamine moiety.
- 25
- 26 12. The compound according to Claim 11, wherein A is amino  
27 or N-alkyl amino having from about 1 to about 4 carbon  
atoms in the alkyl group.
- 28
- 29 13. The compound according to Claim 12, wherein A is amino.
- 30
- 31 14. The compound according to Claim 11, wherein A is a  
32 polyamine moiety having from about 2 to about 12 amine  
33 nitrogen atoms and from about 2 to about 40 carbon  
34 atoms.



01 15. The compound according to Claim 14, wherein A is a  
02 polyamine moiety derived from a polyalkylene polyamine  
03 containing from about 2 to about 12 amine nitrogen  
04 polyamine atoms and from about 2 to about 24 carbon  
05 atoms.

06 16. The compound according to Claim 15, wherein the  
07 polyalkylene polyamine has the formula:  
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13 wherein  $\text{R}_3$  is an alkylene group having from about 2 to  
14 about 6 carbon atoms and  $z$  is an integer from about 1  
15 to about 4.  
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17 17. The compound according to Claim 16, wherein  $\text{R}_3$  is an  
18 alkylene group having from about 2 to about 4 carbon  
19 atoms.  
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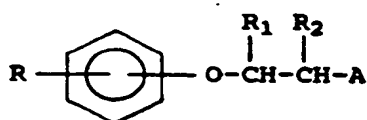
21 18. The compound according to Claim 17, wherein the  
22 polyalkylene polyamine is ethylene diamine or  
23 diethylene triamine.  
24

25 19. The compound according to Claim 18, wherein the  
26 polyalkylene polyamine is ethylene diamine.  
27

28 20. The compound according to Claim 1, wherein R is a  
29 polyalkyl group derived from polyisobutene,  $\text{R}_1$  and  $\text{R}_2$   
30 are hydrogen and A is amino or a polyamine moiety  
31 derived from ethylene diamine.  
32

33 21. A fuel composition comprising a major amount of  
34 hydrocarbons boiling in the gasoline or diesel range

01 and an effective deposit-controlling amount of a  
02 compound of the formula:



10 or a fuel-soluble salt thereof, wherein R is a  
11 polyalkyl group having an average molecular weight in  
12 the range of about 600 to 5,000;

13 R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or lower alkyl  
14 having 1 to 6 carbon atoms; and

15  
16 A is amino, N-alkyl amino having about 1 to about 20  
17 carbon atoms in the alkyl group, N,N-dialkyl amino  
18 having about 1 to about 20 carbon atoms in each alkyl  
19 group, or a polyamine moiety having about 2 to about 12  
20 amine nitrogen atoms and about 2 to about 40 carbon  
21 atoms.

22  
23 22. The fuel composition according to Claim 21, wherein one  
24 of R<sub>1</sub> and R<sub>2</sub> is hydrogen or lower alkyl of 1 to 4  
25 carbon atoms, and the other is hydrogen.

26  
27 23. The fuel composition according to Claim 22, wherein one  
28 of R<sub>1</sub> and R<sub>2</sub> is hydrogen, methyl or ethyl, and the  
29 other is hydrogen.

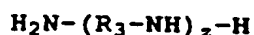
30 24. The fuel composition according to Claim 23, wherein R<sub>2</sub>  
31 is hydrogen, methyl or ethyl, and R<sub>1</sub> is hydrogen.  
32  
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- 01 25. The fuel composition according to Claim 21, wherein R  
02 is a polyalkyl group having an average molecular weight  
03 in the range of about 600 to 3,000.
- 04 26. The fuel composition according to Claim 25, wherein R  
05 is a polyalkyl group having an average molecular weight  
06 in the range of about 700 to 3,000.
- 07  
08 27. The fuel composition according to Claim 26, wherein R<sub>1</sub>  
09 is a polyalkyl group having an average molecular weight  
10 in the range of about 900 to 2,500.
- 11  
12 28. The fuel composition according to Claim 21, wherein R  
13 is a polyalkyl group derived from polypropylene,  
14 polybutene, or a polyalphaolefin oligomer of 1-octene  
15 or 1-decene.
- 16 29. The fuel composition according to Claim 28, wherein R  
17 is a polyalkyl group derived from polyisobutene.
- 18  
19 30. The fuel composition according to Claim 29, wherein the  
20 polyisobutene contains at least about 20% of a  
21 methylvinylidene isomer.
- 22  
23 31. The fuel composition according to Claim 21, wherein A  
24 is amino, N-alkyl amino or a polyamine moiety.
- 25 32. The fuel composition according to Claim 31, wherein A  
26 is amino or N-alkyl amino having from about 1 to about  
27 4 carbon atoms in the alkyl group.
- 28  
29 33. The fuel composition according to Claim 32, wherein A  
30 is amino.
- 31  
32 34. The fuel composition according to Claim 31, wherein A  
33 is a polyamine moiety having from about 2 to about 12  
34

01 amine nitrogen atoms and from about 2 to about 40  
02 carbon atoms.

03 35. The fuel composition according to Claim 34, wherein A  
04 is a polyamine moiety derived from a polyalkylene  
05 polyamine containing from about 2 to about 12 amine  
06 nitrogen polyamine atoms and from about 2 to about 24  
07 carbon atoms.  
08

09 36. The fuel composition according to Claim 35, wherein the  
10 polyalkylene polyamine has the formula:  
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16 wherein  $\text{R}_3$  is an alkylene group having from about 2 to  
17 about 6 carbon atoms and  $z$  is an integer from about 1  
18 to about 4.  
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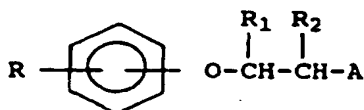
20 37. The fuel composition according to Claim 36, wherein  $\text{R}_3$   
21 is an alkylene group having from about 2 to about 4  
22 carbon atoms.  
23

24 38. The fuel composition according to Claim 37, wherein the  
25 polyalkylene polyamine is ethylene diamine or  
26 diethylene triamine.  
27

28 39. The fuel composition according to Claim 38, wherein the  
29 polyalkylene polyamine is ethylene diamine.  
30

31 40. The fuel composition according to Claim 21, wherein R  
32 is a polyalkyl group derived from polyisobutene,  $\text{R}_1$  and  
33  $\text{R}_2$  are hydrogen and A is amino or a polyamine moiety  
34 derived from ethylene diamine.

- 01 41. The fuel composition according to Claim 21, wherein the  
02 composition contains from about 50 to about 2,000 parts  
03 per million by weight of said compound.
- 04 42. The fuel composition according to Claim 21, where the  
05 composition further contains from about 100 to about  
06 5,000 parts per million by weight of a fuel-soluble,  
07 nonvolatile carrier fluid.
- 08
- 09 43. A fuel concentrate comprising an inert stable  
10 oleophilic organic solvent boiling in the range of from  
11 about 150°F. to 400°F. and from about 10 to about 70  
12 weight percent of a compound of the formula:  
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19 or a fuel-soluble salt thereof, wherein R is a  
20 polyalkyl group having an average molecular weight in  
21 the range of about 600 to 5,000;  
22

23 R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or lower alkyl  
24 having 1 to 6 carbon atoms; and  
25

26 A is amino, N-alkyl amino having about 1 to about 20  
27 carbon atoms in the alkyl group, N,N-dialkyl amino  
28 having about 1 to about 20 carbon atoms in each alkyl  
29 group, or a polyamine moiety having about 2 to about 12  
30 amine nitrogen atoms and about 2 to about 40 carbon  
31 atoms.  
32

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- 01 44. The fuel concentrate according to Claim 43, wherein one  
02 of R<sub>1</sub> and R<sub>2</sub> is hydrogen or lower alkyl of 1 to 4  
03 carbon atoms, and the other is hydrogen.  
04
- 05 45. The fuel concentrate according to Claim 44, wherein one  
06 of R<sub>1</sub> and R<sub>2</sub> is hydrogen, methyl or ethyl, and the  
07 other is hydrogen.  
08
- 09 46. The fuel concentrate according to Claim 45, wherein R<sub>2</sub>  
10 is hydrogen, methyl or ethyl, and R<sub>1</sub> is hydrogen.  
11
- 12 47. The fuel concentrate according to Claim 43, wherein R  
13 is a polyalkyl group having an average molecular weight  
14 in the range of about 600 to 3,000.  
15
- 16 48. The fuel concentrate according to Claim 47, wherein R  
17 is a polyalkyl group having an average molecular weight  
18 in the range of about 700 to 3,000.  
19
- 20 49. The fuel concentrate according to Claim 48, wherein R  
21 is a polyalkyl group having an average molecular weight  
22 in the range of about 900 to 2,500.  
23
- 24 50. The fuel concentrate according to Claim 43, wherein R  
25 is a polyalkyl group derived from polypropylene,  
26 polybutene, or a polyalphaolefin oligomer of 1-octene  
27 or 1-decene.  
28
- 29 51. The fuel concentrate according to Claim 50, wherein R  
30 is a polyalkyl group derived from polyisobutene.  
31
- 32 52. The fuel concentrate according to Claim 51, wherein the  
33 polyisobutene contains at least about 20% of a  
34 methylvinylidene isomer.

- 01 53. The fuel concentrate according to Claim 43, wherein A  
02 is amino, N-alkyl amino or a polyamine moiety.
- 03 54. The fuel concentrate according to Claim 53, wherein A  
04 is amino or N-alkyl amino having from about 1 to about  
05 4 carbon atoms in the alkyl group.  
06
- 07 55. The fuel concentrate according to Claim 54, wherein A  
08 is amino.  
09
- 10 56. The fuel composition according to Claim 53, wherein A  
11 is a polyamine moiety having from about 2 to about 12  
12 amine nitrogen atoms and from about 2 to about 40  
13 carbon atoms.
- 14 57. The fuel concentrate according to Claim 56, wherein A  
15 is a polyamine moiety derived from a polyalkylene  
16 polyamine containing from about 2 to about 12 amine  
17 nitrogen polyamine atoms and from about 2 to about 24  
18 carbon atoms.  
19
- 20 58. The fuel concentrate according to Claim 57, wherein the  
21 polyalkylene polyamine has the formula:  
22  
23
- 24 
$$\text{H}_2\text{N}-(\text{R}_3-\text{NH})_z-\text{H}$$
  
25
- 26
- 27 wherein  $\text{R}_3$  is an alkylene group having from about 2 to  
28 about 6 carbon atoms and  $z$  is an integer from about 1  
29 to about 4.
- 30
- 31 59. The fuel concentrate according to Claim 58, wherein  $\text{R}_3$   
32 is an alkylene group having from about 2 to about 4  
33 carbon atoms.  
34

- 01 60. The fuel concentrate according to Claim 59, wherein the  
02 polyalkylene polyamine is ethylene diamine or  
03 diethylene triamine.  
04
- 05 61. The fuel concentrate according to Claim 60, wherein the  
06 polyalkylene polyamine is ethylene diamine.  
07
- 08 62. The fuel concentrate according to Claim 43, wherein R  
09 is a polyalkyl group derived from polyisobutene, R<sub>1</sub> and  
10 R<sub>2</sub> are hydrogen and A is amino or a polyamine moiety  
11 derived from ethylene diamine.
- 12 63. The fuel concentrate according to Claim 43, wherein the  
13 fuel concentrate further contains from about 20 to  
14 about 60 weight percent of a fuel-soluble, nonvolatile  
15 carrier fluid.  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/07991

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C10L 1/22; C07C 217/64  
US CL : 044/424, 425; 564/353, 354

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 044/424, 425; 564/353, 354

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,778,481 A (COURTNEY) 18 October 1988, column 5, lines 39 to column 6, line 49.	1-63
A	US 4,568,354 A (DAVIS ET AL) 04 February 1986, column 2, lines 5-24.	1-63
A	US 4,392,866 A (SUNG ET AL) 12 July 1983, column 1, lines 26-47.	1-63
A	US 4,259,086 A (MACHLEDER ET AL) 31 March 1981, column 17, lines 57 to column 18, line 2.	1-63
A	US 4,147,641 A (MACHLEDER ET AL) 03 April 1979, column 2, lines 29-64.	1-63
A	US 3,849,083 A (DUBECK) 19 November 1974, column 1, lines 28-37.	1-63

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* "A" document defining the general state of the art which is not considered to be of particular relevance	"T" later documents published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document published on or after the international filing date	"X" documents of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" documents which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" documents of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"A" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
09 JULY 1997

Date of mailing of the international search report  
11 SEP 1997

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